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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

INVENTOR(S)

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☐ *Additional inventors are being named on the ____ separately numbered sheets attached hereto*

TITLE OF THE INVENTION (280 characters max)

THERMOFORMABLE MELT-BONDED MULTILAYER FILMS INCLUDING CYCLOOLEFIN COPOLYMER AND STYRENE-BUTADIENE B LOCK COPOLYMER

Direct all correspondence to: **CORRESPONDENCE ADDRESS**

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☐ Application Data Sheet. See 37 CFR 1.76

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Respectfully submitted,

SIGNATURE [signature] Date 2/23/05

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TYPED or PRINTED NAME Michael W. Ferrell, Esq. Docket Number: 1765 (TI-04-8)

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USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

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Invention: **THERMOFORMABLE MELT-BONDED MULTILAYER FILMS INCLUDING CYCLOOLEFIN COPOLYMER AND STYRENE-BUTADIENE B LOCK COPOLYMER**

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Attorney Docket No. 1765 (TI-04-8)
February 23, 2005

Provisional Patent Application

of:

S. Thomas Lee

for

Thermoformable Melt-Bonded Multilayer Films Including Cycloolefin Copolymer and Styrene-Butadiene Block Copolymer

THERMOFORMABLE MELT-BONDED MULTILAYER FILMS INCLUDING CYCLOOLEFIN COPOLYMER AND STYRENE-BUTADIENE B LOCK COPOLYMER

Technical Field

The present invention relates generally to multilayered films and more particularly to a multilayered film including at least one layer of cyclo-olefin copolymer directly melt-bonded to a layer of styrene-butadiene block copolymer. The film layers may be co-extruded together and melt-bonded to each other without the aid of a tie layer. The multilayered films of the invention exhibit superior peel adhesion, optical properties, and moisture barrier properties. The films thermoform well and are particularly suitable for blister packaging sheet.

Background

Cyclo-olefin copolymers (referred to as COP or COPs) exhibit excellent transparency and moisture permeation properties, in addition to heat resistance, chemical resistance, solvent resistance, and rigidity. COP, a non-crystalline copolymer, has the further advantage of being amenable to thermoforming. While these properties make COP desirable in packaging applications, thermoformed COP is sometimes susceptible to stress cracking when exposed to alkaline environments, especially when high draw ratios are used to make the thermoformed part. A multilayered film incorporating a COP layer can be seen in United States Patent No. 6,042,906 to *Itoh et al.* which discloses a plastic container having a COP layer adhered to an olefin resin or an ethylene/vinyl copolymer layer. The COP layer is adhered to the non-cyclic olefin layers with an adhesive resin.

Styrene-butadiene copolymers (sometimes referred to as SBC or SBCs) are similarly well-known in the art and are sometimes used in packaging films. SBCs generally exhibit good processability, mechanical properties and transparency, but exhibit modest barrier properties. SBCs have been employed in

packaging film or sheet in combination with other polymers including polyvinyl chloride (PVC), polyvinylidene chloride (PVDC), and polypropylene. United States Patent No. 6,517,950 discloses a multilayer film comprising a styrene-butadiene block copolymer and a homogenous ethylene/alpha-olefin layer. SBC/polypropylene films tend to warp when used in blister packaging. Also, due to an increasing demand to make halogen-free packaging PVC and PVDC are not generally desirable polymers to include in packaging films.

Multilayer polymer films or laminates are produced for their aggregate properties, typically including "tie" layers of adhesive materials in the case of multilayer polymer films since different polymers usually do not readily adhere to one another. Tie layers add expense and can adversely effect optical properties as well as processability.

Multilayered polymeric films or sheets may be produced by co-extrusion. Co-extrusion is a well known process. United States Patent Nos. 3,479,425; 3,959,431; and 4,406,547 describe co-extrusion processes whereby multilayered plastic films can be formed. Multilayered films are usually co-extruded by passing two or more melt streams of polymers through a die. The materials are fused together into a layered structure and are allowed to cool. Once extruded, plastic films can be shaped into containers by subjecting them to a thermoforming process. The construction of blister packaging or other articles of manufacture by thermoforming processes is well known.

Thermoforming is credited with producing packaging having high durability and integrity. United States Patent Nos. 4,421,721; 4,994,229; 5,106,567; 6,086,600 describe various thermoforming processes for plastic containers. Generally, a thermoforming process forms plastic containers and packaging structures by heating a sheet of plastic to a desirable forming temperature and shaping the plastic by subjecting it to vacuum or pressure shaping

in a mold. Thermoforming is a preferred method of making plastic containers because it is comparatively faster than other techniques and uses less material.

Thermoformed blister packaging commonly contains commercial articles including food products, personal care products, and the like. United States Patent No. 6,489,016 discloses multilayer packaging films of polyolefin. Also disclosing such packaging materials and packages made therefrom are United States Patent Nos. 6,383,582; 5,750,262; 5,783,270; and 5,755,081. The moisture barrier properties of a film is an important characteristic in packaging applications. Moisture transmission through a container may adversely affect the contents, especially in applications where the packaging contains pharmaceuticals, food products, and the like. Optical properties such as haze and transparency are also important in packaging applications. It is desirable that packaging be clear so that the product is viewable by the customer.

Despite the availability of a vast number of materials, there is still a need, particularly in blister packaging applications, for thermoformable sheet which has suitable moisture barrier properties, clarity, processability and will not stress-crack. It has been unexpectedly found in accordance with the present invention that a multilayered film may be produced by directly melt-bonding a cyclo-olefin copolymer with a styrene-butadiene block copolymer to provide sheet with superior optical properties, interlayer adhesion, durability and processability. It is particularly surprising that the COP and the SBC can be co-extruded together to form a melt-bonded composite film suitable for thermoforming because the two polymers exhibit vastly different viscosities.

Summary of Invention

There is provided in accordance with the present invention a multilayer film comprising a styrene-butadiene block copolymer layer and a cyclo-olefin copolymer layer which is directly melt-bonded to the styrene-butadiene layer. Typically, the cyclo-olefin layer consists essentially of a cyclo-olefin copolymer

and incorporates the residue of a polycyclic olefin or an olefin having a cyclopropene group. Other suitable comonomers include ethylene or propylene. The cyclo-olefin copolymer most preferably includes the residue of norbornene. A preferred cycloolefin copolymer incorporates the residue of norbornene and ethylene, and in especially preferred embodiments the cycloolefin copolymer consists essentially of the residue of norbornene and ethylene. A suitable range of norbonene content is between about 10 to about 70 mol % and a suitable range of ethylene content is about 30 to about 90 mol %. Preferably, the range of nobornene content is between about 25 to about 45 mol % and the ethylene content is preferably between about 55 and about 75 mol %.

The styrene-butadiene layer may consist essentially of at least about 50 wt. % styrene, about 5 to about 50 wt. % butadiene, and optionally up to 10 % other polymeric components. A preferred styrene-butadiene copolymer consists of the residue of styrene and butadiene. A typical range for styrene content is from about 60 to about 90 weight percent and a typical range for butadiene content is from about 10 to about 40 weight percent. More preferably, the styrene content is present in an amount from about 70 to about 80 weight percent and the butadiene is present in an amount from about 20 to about 30 weight percent.

The cyclo-olefin layer is generally at least four times thicker than the styrene-butadiene layer and is preferably at least six times thicker. Anywhere from five to fifteen times thicker may be suitable. A preferred embodiment is wherein the film is a three-layered film where the cyclo-olefin layer is between two styrene-butadiene layers. The styrene-butadiene layer is preferably melt-bonded to the cyclo-olefin layer by means of co-extrusion, but the layers may also be bonded by lamination.

In the films of the present invention, the bonded layers of styrene-butadiene and cycloolefin typically exhibit a peel adhesion value of at least about 0.5 lbf/in. More preferably, the layers exhibit a peel adhesion of at least about 1.0

lbf/in. The films made according to the present invention generally have a correlated haze value of less than about 5 % when the film has a thickness of 0.012 inches.

Also provided in accordance with the present invention is a method for making a multilayer film by co-extruding a styrene-butadiene block copolymer layer and a cyclo-olefin layer, such that the styrene-butadiene layer is directly melt-bonded to the cyclo-olefin layer. Here again, the styrene-butadiene layer preferably consists essentially of at least about 50 weight percent styrene, about 5 to about 50 weight percent butadiene, and optionally up to 10 weight percent of other polymerized components. The cyclo-olefin layer may also consist essentially of a cyclo-olefin copolymer. Typically, the cyclo-olefin is extruded at a polymer exit temperature of about 255°F to about 275°F and the styrene-butadiene layer is extruded at a polymer exit temperature of about 210°F to about 230°F.

In yet another feature of the present invention there is provided blister packaging with a thermoformed blister sheet defining one or more domed receptacle portions, where the blister sheet is thermoformed from a multilayered film which includes a styrene-butadiene layer that is melt bonded to a cyclo-olefin layer. The receptacle portions typically contain tablets, capsules, pills, caplets, or the like which typically comprise pharmaceutical products, medicinal products, vitamins, nutritional supplements, or confections including mints, gum and the like.

Further features and advantages of the present invention will become apparent from the discussion that follows.

Brief Description of Drawings

The invention is described in detail below with reference to the various figures wherein like numerals designate similar parts and wherein:

Figure 1 is a view in perspective of a section of sheet continuously extruded in accordance with the present invention;

Figure 2 is an enlarged cross-sectional view of the sheet in **Figure 1**;

Figure 3 is a cross-sectional view of blister packaging which includes the film of the present invention; and

Figure 3a is an enlarged cross-sectional view of the blister sheet in **Figure 3**.

Detailed Description

The present invention is described in detail below with reference to the various examples and appended Figures. Modifications to particular examples within the spirit and scope of the present invention, set forth in the appended claims, will be readily apparent to those of skill in the art.

Unless otherwise indicated, terms are to be construed in accordance with their ordinary meaning. Following are some exemplary definitions of terms used in this specification and the appended claims.

The terms "film" and "sheet" are used interchangeably. Sheet may be used to refer to film that is thicker than 100 microns in some instances.

As used herein, the phrase "directly melt-bonded" is defined as application of a subject film layer to an object film layer, without a tie layer, adhesive, or other layer in between, where the layers are adhered to one another when in a molten or partially softened state. Typically, the layers are bonded together in their molten form. The subject layer may be melt-bonded to further layers by a co-extrusion process or a lamination process. The layers of the films of the present invention typically exhibit an interlayer peel adhesion strength of greater than 0.5 lbf/in.

As used herein, the phrase "multilayer" or "multilayered" refers to two or more layers, which may be present in any order or combination.

Peel adhesion strength between layers was tested using a modified version of ASTM D903, a method used to measure the 180 degree peel strength of adhesives. According to the test, the rigid member is placed in the upper jaw and the flexible member is bent 180 degrees and held in the lower jaw. Unless otherwise noted, the test is run on a 0.591 in (15 mm) wide specimen, using a 12 ipm test speed, a 1 inch peel start extension and a 6 inch peel end extension. Typically, films made in accordance with the present invention exhibit a peel strength of greater than 0.2 lbf/in and preferably greater than 0.5 lbf/in and even more preferably greater than 1 lbf/in.

Optical haze is tested in accordance with ASTM D1003-00 using films having thicknesses of about 0.012 inches. In the examples below, a spectrophotometer was used to measure the haze values as set forth in Procedure B of ASTM D1003-00. The films of the present invention typically exhibit a correlated haze of less than 5% and preferably less than 3.5%.

The term "styrene-butadiene copolymers," sometimes referred to herein as SBC or SBCs are well known copolymers comprising styrene monomers and butadiene monomers. "Block copolymer" as used herein refers to any polymer

containing repeating sequences of two or more distinct multiatomic units bonded together in a chain. Thus, styrene-butadiene block copolymers typically have a structure that can be represented by poly(styrene-b-butadiene-b-styrene). Styrene-butadiene block copolymers are typically made using anionic polymerization techniques using an alkyllithium initiator. The production of styrene-butadiene block copolymers primarily promotes the polymerization of styrene and butadiene monomers, but additional coupling agents can be interposed within the polymer chain in small amounts. Examples of acceptable coupling agents include alcohols, organohalogens, esters, chlorosilanes, and divinylbenzene. United States Patent No. 4,086,298, the disclosure of which is incorporated herein in its entirety by reference, discloses examples of styrene-butadiene block copolymers and their method of manufacture. Styrene-butadiene copolymers are commercially available; acceptable SBC block copolymers for use in the present invention include Styrolux® 684D, Styrolux®3G55, and Styrolux® 3G33 manufactured by BASF Corporation. The following tables list properties of some Styrolux® copolymers:

Properties of Styrolux® 3G33 and 684D

Property	ISO test method	3G33	684D
Melt Volume Rate (200°C/5) kg, cc/10 min.	1133	12	11
Density (g/cm^3)	1183	1.02	1.01
Izod impact (KJ/m^2) 23°C	180	3.5	4
Vicat Softening Temperature (VST/B/50°C)	306	56	59

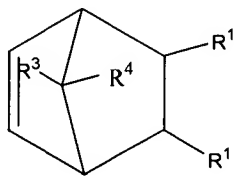
Properties of Styrolux® 3G55 Q420

Property	ASTM Test Method	3G55 Q420
Melt Flow Rate (200 °C/5 kg), g/10 min	D-1238	15
Vicat, B/1 (120 °C/h, 10 N), °C	D-1525	72

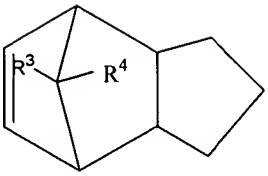
Other commercially available styrene-butadiene copolymers include Kraton™ D-1401P (Shell Chemicals) and Asaflex™ (Asahi Chemical).

Useful cyclo-olefin copolymers, collectively referred to herein as COPs or COP resins are known in the art. For example, United States Patent No. 6,068,936 (Assignee: Ticona GmbH) and United States Patent No. 5,912,070 (Assignee: Mitsui Chemicals, Inc.) disclose several cycloolefin copolymers, the disclosures of which are incorporated herein in their entirety by reference. Cycloolefin copolymers include cyclo-olefin monomers and acyclic olefin monomers, described further below.

Cyclo-olefins are mono- or polyunsaturated polycyclic ring systems, such as cycloalkenes, bicycloalkenes, tricycloalkenes or tetracycloalkenes. The ring systems can be monosubstituted or polysubstituted. Preference is given to cyclo-olefins of the formulae I, II, III, IV, V or VI, or a monocyclic olefin of the formula VII:



(I)



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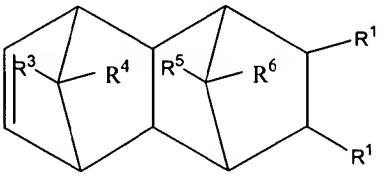

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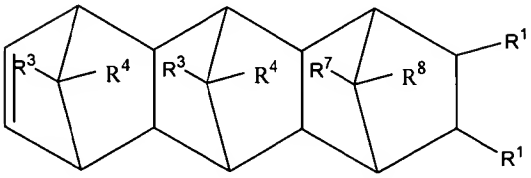

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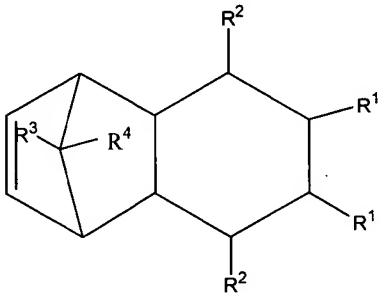

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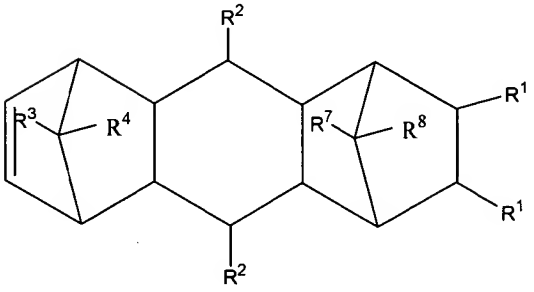

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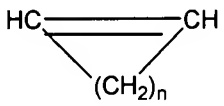


(VII)

wherein R^1, R^2, R^3, R^4, R^5, R^6, R^7 and R^8 are the same or different and are H, a C_6-C_{20} -aryl or C_1 -C_{20} -alkyl radical or a halogen atom, and n is a number from 2 to 10. Examples of such cyclic olefin monomers are norbornene, dimethyl-octahydro-naphthalene, cyclopentene and (5-methyl)norbornene and the like, or

mixtures thereof. These monomers can be made into homopolymer COP or polymerized with acyclic comonomers. Examples of suitable acyclic olefin monomers which may be polymerized with the cyclo-olefins noted above are ethylene, propylene, butylene and the like, or mixtures thereof. A preferred cyclic olefin is norbornene, and a preferred acyclic olefin for reaction therewith is ethylene. Cycloolefin copolymers are commercially available and an acceptable copolymer includes Topas® 8007F04, manufactured by Ticona.

The cycloolefin polymers can be prepared with the aid of transition-metal catalysts, e.g. metallocenes. Suitable preparation processes are known and described, for example, in DD-A-109 225, EP-A-0 407 870, EP-A-0 485 893, United States Patent Nos. 6,489,016, 6,008,298, 6,608,936, and 5,912,070, the disclosures of which are incorporated herein in their entirety by reference. Molecular weight regulation during the preparation can advantageously be effected using hydrogen. Suitable molecular weights can also be established through targeted selection of the catalyst and reaction conditions. Details in this respect are given in the abovementioned specifications.

The films of the present invention may be produced by, for example, co-extrusion techniques. Co-extrusion can be achieved by either (1) introducing the different polymer melt streams, from two or more extruders (one for each resin), in a combining block prior to the extrusion die; or (2) bringing the melt streams together within the die, using a multimanifold die. A multimanifold die is a die that has individual manifolds for each layer. Generally, the individual manifolds are designed to distribute a polymer layer uniformly before combining with other layers either inside or outside the die. Typically, multimanifold dies are flat or annular. Another suitable method for melt-bonding the layers contained in the films of the present invention is lamination. The multilayered films can be laminated by superimposing at least one polymeric layer on another polymeric layer and bonding the layers together while applying heat.

The multilayer films made according to the present invention may comprise two or more layers and may be arranged in various patterns. For example, where A is the styrene-butadiene copolymer and B is the cyclo-olefin copolymer, possible embodiments include A/B/A, B/A/B, B/A, and A/B/A/B/A. The COP layer preferably comprises a core layer between SBC layers. SBC is more suitable as the outer layers because it has a pleasing tactile feel. The present invention also encompasses films having layers of any thickness. Preferably, however, the cyclo-olefin layer has a thickness from between 200-280 μm and the styrene-butadiene layer has a thickness of between 10-50 μm. Overall thicknesses of the film of from about 200-400 microns is particularly suitable for blister packaging sheet.

The films made in accordance with the present invention have the unexpected advantage of superior interlayer adhesion without the aid of an adhesive or tie layer. The absence of a tie layer is advantageous for several reasons. The multilayer film is easier to produce without the additional cost of adhesive or tie material and associated equipment. Tie layers may also impart detrimental optical properties to the film. Furthermore, the absence of a tie layer enables manufacturers with lower extrusion capacity to produce multilayered films in accordance with the present invention. For example, equipment with a maximum extrusion capacity of three layers would be able to produce a three layer SBC/COP/SBC film of the present invention, because no extruder capacity is utilized on the production of a tie layer. The films exhibit a surprisingly high peel adhesion value.

It is also contemplated in accordance with the present invention that the SBC/COP film may be incorporated into a multilayer film, laminate or composite comprising other component layers. Acceptable co-layers can include polyolefins, for example homopolymers or copolymers of C_2-C_{40} α-olefins; polar polymers, for example homopolymers and copolymers of esters, amides, acetates, and anhydrides; and other layers such as paper, cardboard, kraft paper, wood,

metal, metal foils, metallized surfaces, glass, fabric, other fibers, and surfaces coated with substrates such as ink, dye, and the like. It will also be apparent to one ordinarily skilled in the art that additives may be added to one or more layers in the films of the present invention. Acceptable additives include lubricants, dyes, pigments, antioxidants, fillers, processing aids, UV stabilizers, neutralizers, antiblock, or the like; the additives being used at a level that will not change the basic and novel characteristics of tie films, that is, good peel strength and optical clarity.

The multilayer films produced according to the present invention are amenable to thermoforming processes whereby containers and packaging structures are made. "Thermoforming", "thermoformed" and like terminology is likewise given its ordinary meaning. In the simplest form, thermoforming is the draping of a softened sheet over a shaped mold. In the more advanced form, thermoforming is the automatic high speed positioning of a sheet having an accurately controlled temperature into a pneumatically actuated forming station whereby the article's shape is defined by the mold, followed by trimming and regrind collection as is well known in the art. Still other alternative arrangements include the use of drape, vacuum, pressure, free blowing, matched die, billow drape, vacuum snap-back, billow vacuum, plug assist vacuum, reverse draw with plug assist, pressure bubble immersion, trapped sheet, slip, diaphragm, twin-sheet cut sheet, twin-sheet roll-fed forming or any suitable combinations of the above. Details are provided in J.L. Throne's book, *Thermoforming*, published in 1987 by Coulthard. Pages 21 through 29 of that book are incorporated herein by reference. Suitable alternate arrangements also include a pillow forming technique which creates a positive air pressure between two heat softened sheets to inflate them against a clamped male/female mold system to produce a hollow product. Metal molds are etched with patterns ranging from fine to coarse in order to simulate a natural or grain like texturized look. Suitable formed articles are trimmed in line with a cutting die and regrind is optionally reused since the material is thermoplastic in nature. Other arrangements for productivity enhancements

include the simultaneous forming of multiple articles with multiple dies in order to maximize throughput and minimize scrap.

Another method for utilizing film or sheet of the present invention is blow-molding, where a hot parison incorporating the multilayer films of the present invention is expanded against the surfaces of a mold, typically using compressed air or other compressed gases. Articles of manufacture using film or sheet of the present invention can also be produced by extrusion blow molding. Extrusion blow molding employs standard blow molding techniques where the parison is produced by extrusion.

The following examples are intended to be demonstrative of preferred embodiments of the present invention. It will be apparent to those of ordinary skill in the art that many changes can be made to specific embodiments within the scope of the invention.

Example 1 – Co-Extrusion

Using two extruders connected to a multimanifold die, the following resins were co-extruded to produce a continuous multilayer sheet **10** as shown in **Figure 1**.

Resin	Source
Topas® 8007F04	Ticona, LLC
Styrolux 684D	BASF Corporation

Topas® 8007F04 is a cyclo-olefin copolymer contains approximately 36 mol % norbornene monomers, balance ethylene. The Topas® resin was melted in extruder 1 and the Styrolux resin was melted in extruder 2. As stated earlier, Styrolux 684D is a styrene-butadiene block copolymer. It is believed to be approximately 79 wt. % styrene. **Figure 2** is a close-up, cross-sectional view of the continuous sheet shown in **Figure 1**. Referring to **Figures 1** and **2**, film **10**

shows a styrene-butadiene layer **12**, a cyclo-olefin core layer **14**, and another styrene-butadiene layer **16**. The cyclo-olefin copolymer makes up the core layer and has a thickness of about 240 microns. The styrene-butadiene copolymer makes up the two outer layers, each having a thickness of about 30 microns. The multilayer film was extruded under the following conditions:

Cyclo-olefin Extrusion Conditions, Extruder 1

	(°F)
Temperature Zone 1	247
Temperature Zone 2	259
Temperature Zone 3	240
Temperature Zone 4	240
Polymer Exit Temperature	266

Styrene-Butadiene Extrusion Conditions, Extruder 2

	(°F)
Temperature Zone 1	177
Temperature Zone 2	195
Temperature Zone 3	210
Temperature Zone 4	215
Polymer Exit Temperature	219

The films made in accordance with the present invention are particularly suitable to being thermoformed into blister packaging. "Blister packaging" and like terminology refers to packaging that has a blister-like plastic covering that is affixed to a lidding layer which usually contains cardboard. The blister-like region of plastic generally holds items such as pills, tablets, caplets, or capsules. Typically, the objects in the blister packaging are pharmaceutical or medicinal goods, nutritional supplements, vitamins, food, gum, etc. **Fig 3** shows a cross-

section of exemplary thermoformed blister packaging **20** which has a thermoformed blister film sheet **28** including a film of the present invention. The blister packaging also has a lidding sheet **34**. The lidding sheet is a laminate of polyester, aluminum and paper. Other exemplary lidding materials include sheet which comprises rigid foil with a heat-sealable lacquer. The blister sheet is shaped by thermoforming into domes **30, 32** which form receptacle portions to hold items, such as a dosage of medicine, food, etc. **Fig 3a** is an enlarged cross-sectional view of the blister film sheet **28**, illustrating the multilayered structure of the film, having an outer layer **22** of styrene-butadiene copolymer, a core layer **24** of cyclo-olefin copolymer, and an inner layer **26** of styrene-butadiene copolymer. Further discussion of blister packaging appears in United States Patent No. 6,830,153 to *French et al.*, the entirety of which is incorporated herein by reference.

Example 2 – Peel Adhesion

Three films were co-extruded according to the conditions described in Example 1 and tested for peel adhesion using a modified version of ASTM D903. Films 1-3 are all co-extruded, three layer films having the pattern A/B/A where A is the styrene-butadiene layer and B is the cyclo-olefin layer. The A layer was extruded at a thickness of about 30 microns and the B layer was extruded at a thickness of about 240 microns. Each value is an average of five samples.

Peel Adhesion Data

Film ID	Width (in)	A layer	B layer	Peel load (lbf)	Peak load (lbf)	Peak strength (lbf/in)	Peel strength (lbf/in)
1	0.591	Styrolux 3G33	Topas® 8007	0.960	0.997	1.686	1.624
2	0.591	Styrolux 684	Topas® 8007	1.015	1.114	1.885	1.718
3	0.591	Styrolux 3G55-Q420	Topas® 8007	0.436	0.471	0.797	0.738

Example 3 – Optical Haze

Four samples of films were tested of haze in accordance with ASTM D1003-00. Film 1 is a monolayer film of Topas® 8007. Films 2-4 are all co-extruded three layer films having the pattern A/B/A where A is the styrene-butadiene layer and B is the cycloolefin layer. The A layer was extruded at a thickness of 30 microns and the B layer was extruded at a thickness of 240 microns. Films 2-4 were co-extruded according to the conditions in Example 1.

Haze Data

Film ID	Total thickness (in)	A layer	B layer	Correlated Haze (%)
1	0.01	N/A	Topas® 8007	0.4
2	0.012	Styrolux 3G33	Topas® 8007	4.2
3	0.012	Styrolux 684D	Topas® 8007	2.6
4	0.013	Styrolux 3G55	Topas® 8007	3.1

While the invention has been described in connection with numerous examples and illustrative packaging,, modifications to the examples and additional applications within the spirit and scope of the invention will be readily apparent to those of skill in the art. In view of the foregoing discussion, relevant knowledge in the art and references discussed above in connection with the Background and Detailed Description, the disclosures of which are all incorporated herein by reference, further description is deemed unnecessary.

WHAT IS CLAIMED IS:

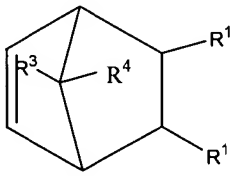
1. A multilayer film comprising:

a styrene-butadiene block copolymer layer; and

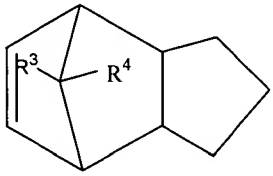
a cyclo-olefin copolymer layer which is directly melt-bonded to the styrene-butadiene block copolymer layer.

2. The multilayer film of Claim 1, wherein said cyclo-olefin copolymer layer consists essentially of a cyclo-olefin copolymer.

3. The multilayer film of Claim 1, wherein said cyclo-olefin copolymer incorporates the residue of (i) the polycyclic structure of formula I, II, III, IV, V or VI, or (ii) the monocyclic structure of the formula VII:



(I)



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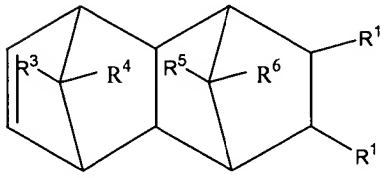

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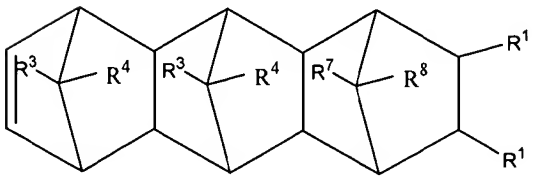

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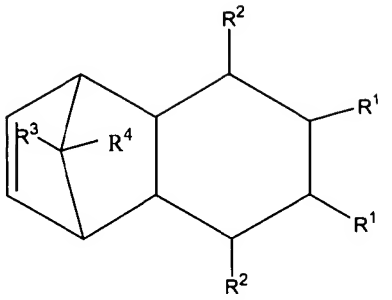

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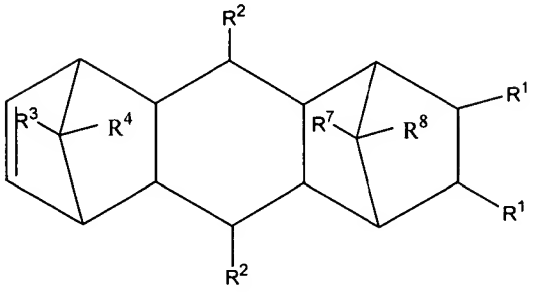
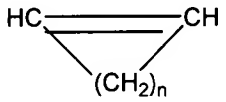


(VI)



(VII)

wherein R^1, R^2, R^3, R^4, R^5, R^6, R^7 and R^8 are the same or different and are H, a C_6-C_{20} -aryl or C_1 -C_{20} -alkyl radical or a halogen atom, and n is a number from 2 to 10.

4. The multilayer film of Claim 3, wherein said cyclo-olefin copolymer includes the residue of ethylene or propylene.

5. The multilayer film of Claim 4, wherein said cyclo-olefin copolymer incorporates the residue of norbornene.

6. The multilayer film of Claim 5, wherein said cyclo-olefin copolymer is a copolymer of norbornene and ethylene.

7. The multilayer film of Claim 6, wherein said cyclo-olefin copolymer consists essentially of the residue of norbornene and ethylene.

8. The multilayer film of Claim 7, wherein said cyclo-olefin copolymer comprises between about 10 and about 70 mol % norbornene residue and between about 30 and about 90 mol % percent ethylene residue.

9. The multilayer film of Claim 8, wherein said cyclo-olefin copolymer comprises between about 25 and about 45 mol % norbornene monomer and between about 55 and about 75 mol % ethylene monomer.

10. The multilayer film of Claim 1, wherein said styrene-butadiene block copolymer layer consists essentially of (i) at least about 50 wt. % styrene residue; and (ii) from about 5 to about 50 wt. % butadiene residue; and (iii) optionally up to 10 wt. % other polymeric components.

11. The multilayer film of Claim 1, wherein the styrene-butadiene block copolymer consists of the residue of styrene and butadiene.

12. The multilayer film of Claim 1, wherein the styrene-butadiene block copolymer comprises from about 60 to about 90 wt. % styrene residue and from about 10 to about 40 wt. % butadiene residue.

13. The multilayer film of Claim 1, wherein the styrene-butadiene block copolymer comprises from about 70 to about 80 wt. % styrene residue and from about 20 to about 30 wt. % butadiene residue.

14. The mulilayer film of Claim 1, wherein the cyclo-olefin layer is at least four times thicker than the styrene-butadiene layer.

15. The multilayer film of Claim 1, wherein the cyclo-olefin layer is at least six times thicker than the styrene-butadiene layer.

16. The multilayered film of Claim 1, wherein said film has at least three layers, and wherein the cyclo-olefin layer is present as a core layer between two styrene-butadiene layers.

17. The multilayer film of Claim 1, wherein said styrene-butadiene layer is directly melt-bonded to the cyclo-olefin layer by co-extrusion.

18. The multilayer film of Claim 1, wherein said styrene-butadiene layer is melt-bonded to the cyclo-olefin layer by lamination.

19. The multilayer film of Claim 1, wherein the cyclo-olefin layer is directly melt-bonded to the styrene-butadiene layer such that the layers exhibit a peel adhesion of at least about 0.5 lbf/in.

20. The multilayer film of Claim 1, wherein the cyclo-olefin layer is directly melt-bonded to the styrene-butadiene layer such that the layers exhibit a peel adhesion of at least about 1.0 lbf/in.

21. The multilayer film of Claim 1, wherein said film has a correlated haze of less than about 5 % at a thickness of 0.012 inches.

22. A method for making a multilayer film comprising co-extruding a styrene-butadiene block copolymer layer with a cyclo-olefin copolymer layer, such that the styrene-butadiene block copolymer layer is directly melt-bonded to the cyclo-olefin layer.

23. The method of Claim 22 wherein said styrene-butadiene layer consists essentially of: (i) at least about 50 wt. % styrene residue; (ii) from about 5 to about 50 wt. % butadiene residue; and (iii) optionally up to 10 wt. % other polymeric components.

24. The method of Claim 22, where said cyclo-olefin layer consists essentially of a cyclo-olefin copolymer.

25. The method of claim 22 further comprising extruding the cyclo-olefin layer at a polymer exit temperature of about 255°F to about 275°F, and extruding the styrene-butadiene layer at a polymer exit temperature of about 210°F to about 230°F.

26. Blister packaging having a thermoformed blister sheet defining one or more domed receptacle portions, wherein the blister sheet is thermoformed from a multilayer film which includes a styrene-butadiene block copolymer layer that is directly melt-bonded to a cyclo-olefin copolymer layer.

27. The blister packaging of Claim 26, wherein said domed receptacle portion contains tablets, capsules, pills, caplets or the like.

28. The blister packaging of Claim 26, wherein said domed receptacle portion contains a product selected from the group consisting of pharmaceutical products, medicinal products, vitamins, nutritional supplements, and confections.

ABSTRACT

A packaging film or sheet having a styrene-butadiene block copolymer directly melt-bonded to at least one layer of a cyclo-olefin copolymer is disclosed. The films may be made by means of co-extrusion. The packaging film is amenable to thermoforming processes and is particularly suitable for forming blister packaging used in pharmaceutical applications.

FIG. 1

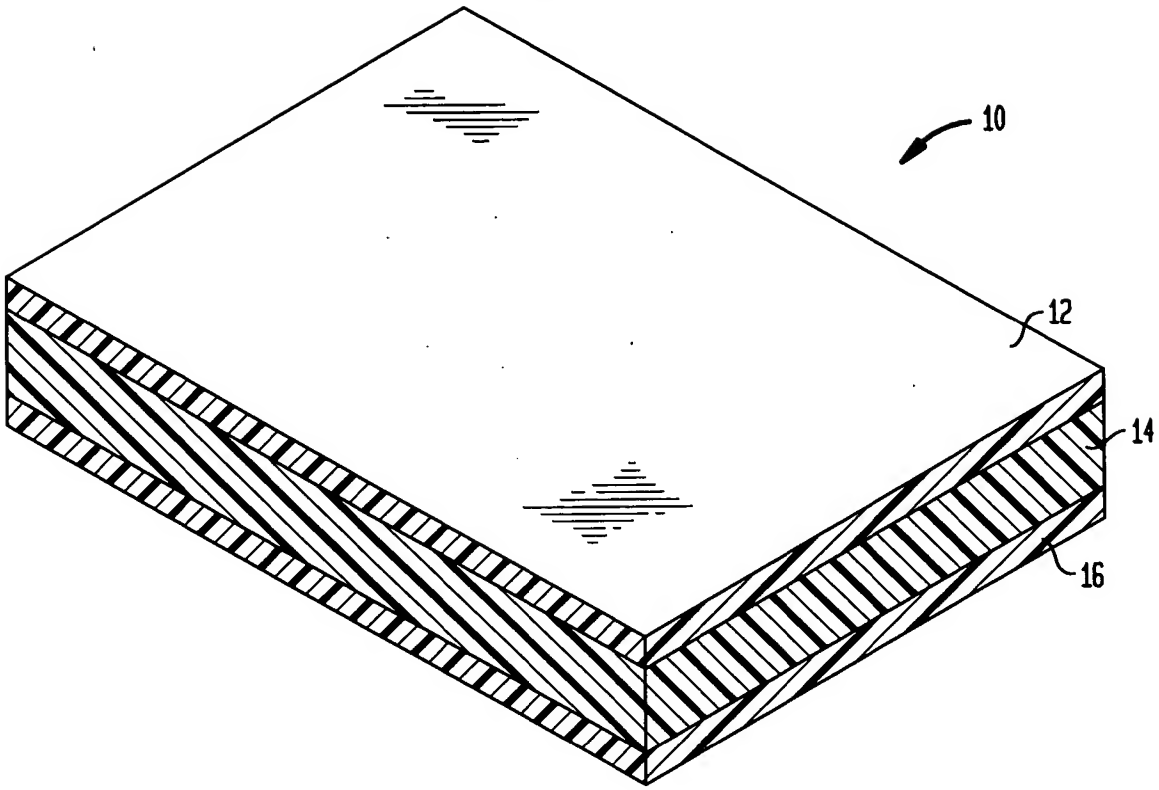


FIG. 2

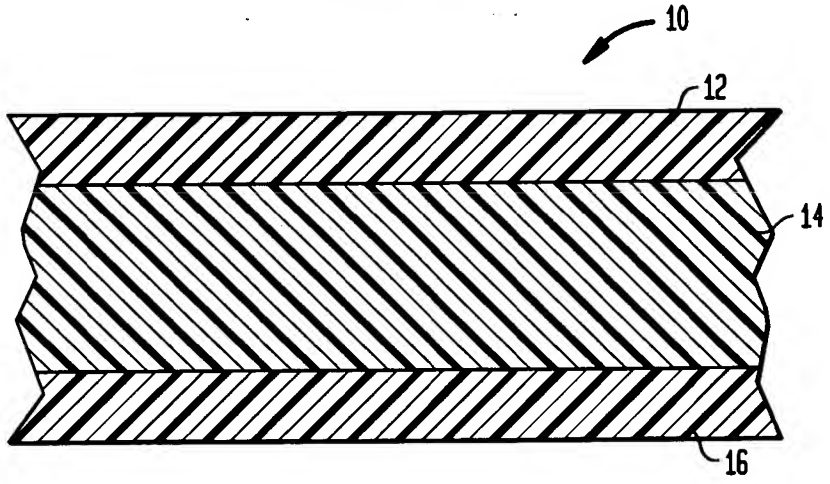


FIG. 3

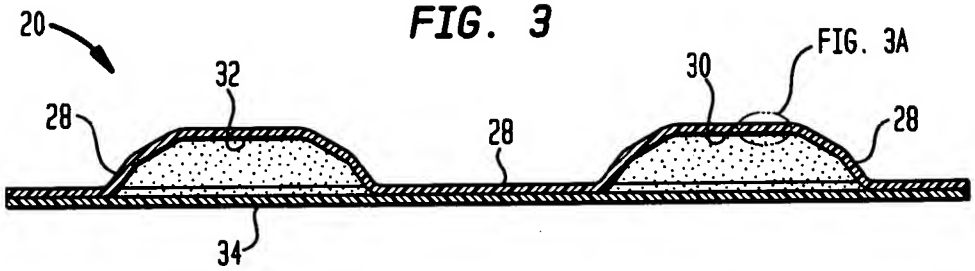
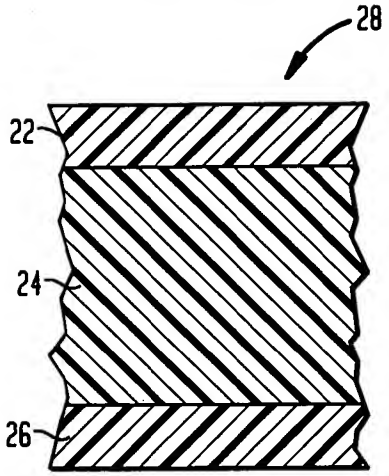


FIG. 3A



Docket No.
1765 (TI-04-8)

Declaration and Power of Attorney For Patent Application

English Language Declaration

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

THERMOFORMABLE MELT-BONDED MULTILAYER FILMS INCLUDING CYCLOOLEFIN COPOLYMER AND STYRENE-BUTADIENE B LOCK COPOLYMER

the specification of which

(check one)

☒ is attached hereto.

☐ was filed on _____ as United States Application No. or PCT International Application Number _____

and was amended on _____

(if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR 1.56, including for continuation-in-part applications, material information which became available between the filing date of the prior application and the national or PCT international filing date of the continuation-in-part application.

I hereby claim foreign priority benefits under 35 U.S.C. 119(a)-(d) or (f), or 365(b) of any foreign application(s) for patent, or plant breeder's rights certificate(s), or 365(a) of any PCT International application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent, inventor's or plant breeder's rights certificate(s), or any PCT international application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application(s)			Priority Claimed
_____ (Number)	_____ (Country)	_____ (Day/Month/Year Filed)	☒
_____ (Number)	_____ (Country)	_____ (Day/Month/Year Filed)	☒
_____ (Number)	_____ (Country)	_____ (Day/Month/Year Filed)	☒

I hereby claim the benefit under 35 U.S.C. Section 119(e) of any United States provisional application(s) listed below:

(Application Serial No.)	(Filing Date)

I hereby claim the benefit under 35 U. S. C. Section 120 of any United States application(s), or Section 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. Section 112, I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, C. F. R., Section 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application:

(Application Serial No.)	(Filing Date)	(Status) (patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. *(list name and registration number)*

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Citizenship
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